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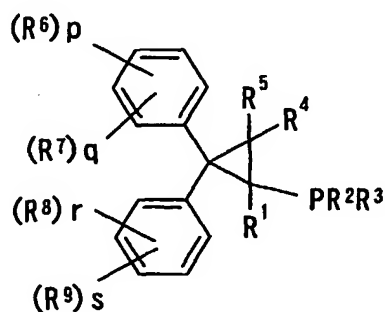
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[Continued on next page]

(54) Title: PHOSPHINE COMPOUND, INTERMEDIATE, PALLADIUM-COMPLEX, AND USE THEREOF



(1)

(57) Abstract: Palladium-phosphine complexes obtained by reacting a 5 compound of formula (1) below with a palladium compound: (wherein R<sup>1</sup> is a hydrogen atom, an alkyl group, a cycloalkyl group or a phenyl group which may be substituted; R<sup>2</sup> and R<sup>3</sup> are each, the same or different, an alkyl group, a cycloalkyl group or a phenyl group which may be substituted; R<sup>4</sup> and R<sup>5</sup> are each, the same or different, a hydrogen atom, an alkyl group, a cycloalkyl group or a phenyl group which may be substituted; R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> are each, the same or different, an alkyl group, a cycloalkyl group, a phenyl group which may be substituted, an alkoxy group, a dialkylamino group, a halogen atom, a phenyl group, a benzyl group, a naphthyl group or a halogenated alkyl

group; R<sup>6</sup> and R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> may be combined to form, each, a fused ring, a trimethylene group, a tetramethylene group or a 20 methylenedioxy group; p, q, r and s are each an integer of 0 to 5; and p + q, and r + s are each in the range of 0 to 5.), which is a novel and efficient catalyst for manufacturing various useful compounds.



— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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## A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TOPOLSKI, M. ET AL: "Chiral carbenoids: their formation and reactions" JOURNAL OF ORGANIC CHEMISTRY (1993), 58(3), 546-55, 1993, XP002279592 the whole document	11
X	WALBORSKY, H. M. ET AL: "Carbenoids. Metal assisted ionization" TETRAHEDRON LETTERS (1985), 26(23), 2743-6 1985, XP002279593 the whole document	11

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BOCHE, G. ET AL: "Alternative pathways in the reactions of cyclopropyl halides with alkali metal naphthalenes" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (1980), 102(17), 5697-9 , 1980, XP002279594 the whole document ---	11
X	LUCKENBACH, REINER ET AL: "Electrocyclic ring opening of cyclopropyl halides in the course of their reaction with sodium iodide in acetone" ZEITSCHRIFT FUER NATURFORSCHUNG, TEIL B: ANORGANISCHE CHEMIE, ORGANISCHE CHEMIE (1979), 34B(3), 464-80 , 1979, XP008030602 the whole document ---	11
X	SANDER, VOLKER ET AL: "Synthesis and reactions of 1-chloro-1-cyclopropanecarboxylic acids and 1-cyclopropene-1-carboxylic acids" CHEMISCHE BERICHTE (1978), 111(12), 3879-91 , 1978, XP008030603 the whole document ---	11
X	WALBORSKY, H. M. ET AL: "Cyclopropanes. XXXIII. Reaction of lithium metal surfaces with optically active 1-halo-1-methyl-2,2-diphenylcyclopropane" JOURNAL OF ORGANOMETALLIC CHEMISTRY (1973), 51, 55-75 , 1973, XP002279597 the whole document ---	11
X	WALBORSKY, H. M. ET AL: "Cyclopropanes. XXXII. Mechanism of Grignard formation" JOURNAL OF ORGANOMETALLIC CHEMISTRY (1973), 51, 31-53 , 1973, XP002279598 the whole document ---	11
X	WALBORSKY, HARRY M. ET AL: "Cyclopropanes. XXIX. Stereochemistry of the 1-methyl-2,2- diphenylcyclopropyl radical in and out of solvent cage" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (1971), 93(3), 671-5 , 1971, XP002279599 the whole document ---	11

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International Application No.  
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HAUSSER, JACK W. ET AL: "Solvolysis of cyclopropyl halides. 2-Phenylcyclopropyl chlorides" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (1967), 89(26), 6981-4 , 1967, XP002279600 the whole document ---	11
P,X	IKEDA, HIROSHI ET AL: "Spectroscopic and Calorimetric Studies on the Mechanism of Methylenecyclopropane Rearrangements Triggered by Photoinduced Electron Transfer" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (2003), 125(30), 9147-9157 , 2003, XP002279601 the whole document -----	11